

Ab-Initio Molecular Dynamics

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Computer simulations and molecular dynamics in particular, is a very powerful method to provide detailed and essentially exact informations of classical many-body problems. With the advent of *ab-initio* molecular dynamics, where the forces are computed on-the-fly by accurate electronic structure calculations, the scope of either method has been greatly extended. This new approach, which unifies Newton's and Schrödinger's equations, allows for complex simulations without relying on any adjustable parameter. This review is intended to outline the basic principles as well as a survey of the field. Beginning with the derivation of Born-Oppenheimer molecular dynamics, the Car-Parrinello method as well as novel hybrid scheme that unifies best of either approach are discussed. The predictive power is demonstrated by a series of applications ranging from insulators to semiconductors and even metals in condensed phases.

INTRODUCTION

The geometric increase in performance of computers over last few decades, together with advances in applied physics and mathematics has led to the birth of a new way of doing science that is in the intersection of theory as well as experiment. As a consequence, they are referred to as computational sciences and allow for computer experiments under perfectly controllable and reproducible conditions. In this way computer simulations have been very successful in explaining a large variety of physical phenomena and guiding experimental work. In addition it is even possible to predict new phenomena by conducting experiments *in silico* that otherwise would be too difficult, expensive, or simply impossible to perform. However, the by far most rewarding outcome of computer simulations is the invaluable insight they provide into the behavior and the dynamics of a system. The two most common algorithms for such studies are the Monte Carlo (MC) [1] and Molecular Dynamics (MD) [2–4] algorithm. The latter is simply the numerical solution of Newton's equation of motion, which allows both equilibrium thermodynamic and dynamical properties of a system at finite temperature to be computed. Since it also provides a 'window' onto the atomic real-time evolution of the atoms, another role of MD is that of a computational microscope.

One of the most challenging, but very important aspects of MD simulations is the calculation of the interatomic forces. In classical simulations, they are computed from empirical potential functions, which have been parametrized to reproduce experimental or accurate *ab-initio* data on small model systems. Even though great strides in elaborating these empirical potentials have been made, often the transferability to systems or regions of the phase diagram different from the ones to which they have been fitted is restricted. Furthermore, they are not able to simulate with sufficient predictive power chemical bonding processes that take place

in many relevant systems. Eventually, some of the most important and interesting phenomena of modern physics and chemistry are intrinsically nonclassical.

Therefore, a first-principles based approach, such as *ab-initio* molecular dynamics (AIMD) [5], where the forces are calculated on-the-fly from accurate electronic structure calculations, is very attractive since many of these limitations can in principle be removed. However, the increased accuracy and predictive power of AIMD simulations comes at significant computational cost. For this reason, density functional theory (DFT) [6] is to date the by far most commonly employed electronic structure theory, but it is important to note that AIMD is a general concept that in principle can be used in conjunction with any electronic structure method. Nevertheless, also the *ab-initio* approach is not without problems - the relevant energy scale is tiny, well below $k_B T$, and in particular the attainable length and time scales are still one of its major limitations.

MOLECULAR DYNAMICS

The mathematical task of MD is to evaluate the expectation value $\langle \mathcal{O} \rangle$ of an arbitrary operator $\mathcal{O}(\mathbf{R}, \mathbf{P})$ with respect to the configurational Boltzmann distribution

$$\langle \mathcal{O} \rangle = \frac{\int d\mathbf{R} d\mathbf{P} \mathcal{O}(\mathbf{R}, \mathbf{P}) e^{-\beta E(\mathbf{R}, \mathbf{P})}}{\int d\mathbf{R} d\mathbf{P} e^{-\beta E(\mathbf{R}, \mathbf{P})}}, \quad (1)$$

where $\beta = 1/k_B T$ is the inverse temperature. The total energy function

$$E(\mathbf{R}, \mathbf{P}) = \sum_{I=1}^{N_{ion}} \frac{\mathbf{P}_I^2}{2M_I} + \Phi(\mathbf{R}_I), \quad (2)$$

where the first term denotes the nuclear kinetic energy, $\Phi(\mathbf{R}_I)$ the potential energy function, N_{ion} the number of

ions and M_I the corresponding masses, depends itself on nuclear positions \mathbf{R} and momenta \mathbf{P} .

One way to evaluate Eq. (1), at least in principle, is to directly solve such a high dimensional integral, whose integrand is very sharply peaked in many dimensions, by an uniform sampling using the MC algorithm. However, such an MC algorithm is very inefficient, if it would not be for importance sampling [1], which satisfies the sufficient detailed balance condition by rejections.

On the other hand, assuming the ergodicity hypothesis, the thermal average $\langle \mathcal{O} \rangle$ can not only be determined as the ensemble average of a MC simulation, but using MD equally as a temporal average

$$\langle \mathcal{O} \rangle = \lim_{\mathcal{T} \rightarrow \infty} \frac{1}{\mathcal{T}} \int dt \mathcal{O}(\mathbf{R}(t), \mathbf{P}(t)). \quad (3)$$

However, by propagating the classical many-body system in time according to Newton's equation of motion, the ions are treated only classical, an usually negligible approximation except for very light atoms or low temperature, where nuclear quantum effects may be important and a quantum formalism such as imaginary-time path integrals [7, 8] is required.

Similar to MC, within MD some kind of importance sampling is naturally performed by preferentially visiting phase space of low potential energy. Furthermore, as denoted by the additional time dependence in Eq. (3), MD allows for additional insights from the ionic real-time evolution, at least in an statistical average sense. It is neither the intention, nor possible, to obtain "exact" trajectories by MD due to the infamous Lyapunov instability, which states that slightly perturbed trajectories are intrinsically exponentially diverging with time.

The equipartition theorem

$$\left\langle \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \right\rangle = \frac{3}{2} k_B T, \quad (4)$$

where M_I is the atomic mass, k_B the Boltzmann constant and T the instantaneous temperature, offers an elegant way to bridge the gap between molecular mechanics and thermodynamics. This opens the door to extract a vast variety of relevant static and dynamic, as well as transport properties from a MD simulation.

Nevertheless, any computational resource is finite, which limits the time and length scales accessible by computer simulations. One way to partially bridge the gap between the microscopic size of the simulated system and the macroscopic reality is to introduce periodic boundary conditions. In this way surface effects are eliminated by effectively simulating an infinite system, albeit with a finite periodicity that is identical with the length L of the simulation cell. As a consequence, only phenomena whose characteristic correlation length is much

smaller than L can be simulated. By similar means only processes whose typical relaxation time is significantly smaller than the simulation time \mathcal{T} can be studied. Even though great strides have been made to extend the time and length scales, it is apparent that techniques such as those reviewed here are clearly needed.

AN *AB-INITIO* POTENTIAL

In AIMD the forces $\mathbf{F}_I = -\nabla_{\mathbf{R}_I} \Phi(\mathbf{R}_I)$ are determined on-the-fly using first principles electronic structure methods. That means that AIMD is not relying on any adjustable parameter, but only on \mathbf{R}_I , which constitutes its predictive power. However, finding the antisymmetric ground state eigenfunctions ψ_0 of the corresponding many-body Hamiltonian at each MD step comes at a significant computational cost, which has to be carefully balanced against the size and sampling requirements of MD.

The Many-Body Schrödinger Equation

Applying the so called Born-Oppenheimer approximation [9], which we have implicitly assumed in the preceding subsection, $\Phi(\mathbf{R}_I)$ can be written as

$$\Phi(\mathbf{R}_I) = \langle \psi_0 | \mathcal{H}_e(\{\mathbf{r}_i\}; \mathbf{R}_I) | \psi_0 \rangle + E_{II}(\mathbf{R}_I), \quad (5)$$

where $\mathcal{H}_e(\{\mathbf{r}_i\}; \mathbf{R}_I)$ is the electronic many-body Hamiltonian, that depend on the electronic coordinates $\{\mathbf{r}_i\}$ and parametrically on \mathbf{R}_I . Essentially, the Born-Oppenheimer approximation allows for a *product ansatz* of the total wavefunction consisting of the nuclear and electronic wavefunctions. Due to the large separation of the nuclear and electronic masses, the electrons can be expected to be in its instantaneous equilibrium with the much heavier nuclei, so that the electronic subsystem can be treated independently at constant \mathbf{R}_I . Nevertheless, we are left with a formidable task to solve the electronic, nonrelativistic, time-independent, many-body Schrödinger equation

$$\mathcal{H}_e(\{\mathbf{r}_i\}; \mathbf{R}_I) \psi_0(\{\mathbf{r}_i\}) = \varepsilon_0(\mathbf{R}_I) \psi_0(\{\mathbf{r}_i\}), \quad (6)$$

which is a high-dimensional, non-linear eigenvalue problem, with eigenfunctions $\psi_0(\{\mathbf{r}_i\})$ and eigenvalues $\varepsilon_0(\mathbf{R}_I)$, respectively.

To visualize the complexity of Eq. (6) let us consider the following *Gedankenmodell* to represent the solution $\psi_0(\{\mathbf{r}_i\})$ on a real-space grid, where each coordinate is discretized by as less as 100 mesh points. Ignoring spin and taking $\psi_0(\{\mathbf{r}_i\})$ to be real, for N_e electrons 10^{6N_e} grid points are required, so that the solution of a single

Si atom would require more grid points than the number of electrons in the whole universe, not to mention solving such a large non-linear eigenvalue problem.

Density Functional Theory

Fortunately, this curse of dimensionality can be ingeniously bypassed by the use of DFT, which is based on two celebrated papers of Hohenberg, Kohn and Sham [6, 10]. The former, the so called Hohenberg-Kohn (HK) theorem, proves the existence of an one-to-one mapping between the ground state density $\rho_0(\mathbf{r})$ and an external potential $v(\mathbf{r})$. In this vain, $\rho_0(\mathbf{r})$, which depends on just 3 electronic degrees of freedom, is designated as the principal quantity rather than the $3N_e$ -dimensional many-body wavefunction. As a consequence, the nondegenerate ground state wavefunction $\psi_0(\{\mathbf{r}_i\}) = \psi[\rho_0(\mathbf{r})]$ and likewise $\mathcal{H}_e[\rho_0(\mathbf{r})]$ are both unique functionals of $\rho_0(\mathbf{r})$, just as the ground state energy $E_0 = E^{\text{DFT}}[\rho_0(\mathbf{r})] = \langle \psi[\rho_0(\mathbf{r})] | \mathcal{H}_e[\rho_0(\mathbf{r})] | \psi[\rho_0(\mathbf{r})] \rangle$. The latter obeys the variational property

$$E^{\text{DFT}}[\rho_0] = \langle \psi_0 | \mathcal{H}_e | \psi_0 \rangle \leq \langle \psi' | \mathcal{H}_e | \psi' \rangle = E^{\text{DFT}}[\rho'], \quad (7)$$

for which equality holds if and only if $\rho_0 = \rho'$. As a consequence Eq. (6) can not only be solved by iteratively diagonalizing $\mathcal{H}_e[\rho]$ within a self-consistent field (SCF) procedure, but equally by minimizing the quantum expectation value of $\mathcal{H}_e[\rho]$:

$$\begin{aligned} E^{\text{DFT}}[\rho_0] &= \min_{\psi} \langle \psi | \mathcal{H}_e | \psi \rangle = \min_{\rho} \langle \psi[\rho] | \mathcal{H}_e[\rho] | \psi[\rho] \rangle \quad (8a) \\ &= \min_{\rho} E^{\text{DFT}}[\rho]. \quad (8b) \end{aligned}$$

In principle the minimization have to be performed under the constraint that $\rho(\mathbf{r})$ is N -representable, i.e. that it is arising from an antisymmetric N -body wavefunction $\psi(\{\mathbf{r}_i\})$. Luckily, this had been solved, and it can be demonstrated that any single-particle density can be written in terms of an antisymmetric many-body wavefunction [11, 12]. On the contrary, for the v -representability problem, which states that $\rho(\mathbf{r})$ is the ground state density of a local potential $v(\mathbf{r})$, no such general solution is known. The HK theorem just guarantees that there cannot be more than one potential for each density, but does not exclude the possibility that there is no potential realizing that density. It is only known for discretized systems that every density is interacting ensemble v -representable. Interestingly, the constructive proof of Levy and Lieb [13, 14] shows that for an interacting system v -representability is not required for the proof of the HK theorem.

For the sake of simplicity in the following I will throughout assume atomic units and confine myself to the physical relevant coulomb system, for which

$$\mathcal{H}_e = \frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I,i} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (9a)$$

$$= \hat{T} + \hat{U} + \hat{V}, \quad (9b)$$

where \hat{T} is the kinetic energy operator of the electrons, while \hat{U} is the electron-electron interaction and $\hat{V} = \sum_i v(\mathbf{r}_i)$ the electron-ion operator. The former two operators are universal and independent of the system, while the latter is system dependent, or nonuniversal. DFT explicitly recognizes that it is indeed the potential $v(\mathbf{r})$, which distinguishes nonrelativistic Coulomb systems and offers a prescription how to deal with \hat{T} and \hat{U} once and for all [15]. Hence, even at this stage based using nothing but the HK theorem DFT is already of some practical use without having to solve the many-body Schrödinger equation and without having to make a single-particle approximation. In principle it should be even possible to calculate all observables, since the HK theorem guarantees that they are all functionals of $\rho(\mathbf{r})$. Presuming the availability of physical sound and accurate approximations one can write

$$E^{\text{DFT}}[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + U[\rho(\mathbf{r})] + V[\rho(\mathbf{r})]. \quad (10)$$

In the so called Thomas-Fermi (TF) approximation [16, 17] the full electron-electron interaction energy is approximated by the Hartree energy

$$U[\rho(\mathbf{r})] \approx U_H[\rho(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (11)$$

that is the electrostatic interaction energy of $\rho(\mathbf{r})$. In addition the kinetic energy is approximated as

$$T[\rho(\mathbf{r})] \approx \int d\mathbf{r} t^{\text{hom}}(\rho(\mathbf{r})) = T^{\text{LDA}}[\rho(\mathbf{r})], \quad (12)$$

where $t^{\text{hom}}(\rho(\mathbf{r}))$ is the kinetic-energy density of a homogeneous interacting system, which is also known as the local-density approximation (LDA). Due to the fact that the explicit form of $t^{\text{hom}}(\rho(\mathbf{r}))$ is only known for a non-interacting system, $t^{\text{hom}}(\rho(\mathbf{r}))$ is further estimated by the single-particle approximation $t_s^{\text{hom}}(\rho(\mathbf{r}))$, i.e.

$$T^{\text{LDA}}[\rho(\mathbf{r})] \approx \int d\mathbf{r} t_s^{\text{hom}}(\rho(\mathbf{r})) = T_s^{\text{LDA}}[\rho(\mathbf{r})]. \quad (13)$$

In the end the TF energy functional

$$E^{\text{TF}}[\rho(\mathbf{r})] = T_s^{\text{LDA}}[\rho(\mathbf{r})] + U_H[\rho(\mathbf{r})] + V[\rho(\mathbf{r})] \quad (14)$$

implies not only the single-particle approximation to the full electron-electron interaction, but also the single-particle mean-field approximation $T_s^{\text{LDA}}[\rho(\mathbf{r})]$ to the exact kinetic energy of the inhomogeneous interacting system. As a consequence, all many-body correlation effects are neglected.

However, the HK theorem predicates that they are again a functional of $\rho(\mathbf{r})$. The addition of an approximation to the exact exchange and correlation (XC) energy results in a formally exact theory, which is referred to as orbital-free DFT [18]. It is therefore important to recognize, that the HK theorem is nothing but the formal exactification of the TF approximation.

Similarly, the Kohn-Sham (KS) [10] scheme can be considered as the exactification of the self-consistent Hartree equations (HE) [19], which differs only in the kinetic energy from the TF approximation. In fact, for the fictitious non-interacting system the kinetic energy is known exactly, even though only in terms of an explicit single-particle orbital functional, i.e. as an implicit density functional

$$T_s[\rho(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^{N_e} \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \quad (15a)$$

$$= T_s[\{\psi_i[\rho(\mathbf{r})]\}]. \quad (15b)$$

Here the fictitious single-particle orbitals, or simply KS orbitals, are denoted as $\psi_i(\mathbf{r})$. As we will see immediately they are eigenfunctions of a fictitious system, known as the KS system. It therefore should be noted that they differ from the single-particle orbitals used in wavefunction based methods and have no strict physical meaning, with two notable exceptions: at the presence of the exact XC functional for the special case of an isolated system with $v(\infty) = 0$ (i) the highest occupied eigenvalue ε_N can be shown to be the negative of the exact, many-body, first ionization potential including relaxation effects, and (ii) that the lowest unoccupied eigenvalue ε_{N+1} is the negative of the electron affinity. Beside these two exceptions, only the density has a real physical meaning and can be written in terms of $\psi_i(\mathbf{r})$ as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_{occ}} f_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}), \quad (16)$$

where N_{occ} is the number of occupied orbitals and f_i the occupation number of state i , so that

$$\sum_{i=1}^{N_{occ}} f_i = N_e. \quad (17)$$

Therewith, the KS energy functional is simply given by

$$E^{\text{KS}}[\rho(\mathbf{r})] = E^{\text{KS}}[\{\psi_i[\rho(\mathbf{r})]\}] = T_s[\{\psi_i[\rho(\mathbf{r})]\}] + U_H[\rho(\mathbf{r})] + V[\rho(\mathbf{r})] + E_{\text{XC}}[\rho(\mathbf{r})] \quad (18a)$$

$$= -\frac{1}{2} \sum_{i=1}^N f_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + E_{\text{XC}}[\rho(\mathbf{r})], \quad (18b)$$

where $E_{\text{XC}}[\rho(\mathbf{r})] = (T[\rho(\mathbf{r})] - T_s[\{\psi_i[\rho(\mathbf{r})]\}]) + (U[\rho(\mathbf{r})] - U_H[\rho(\mathbf{r})])$ is the already mentioned and apparently unknown XC energy functional, whereas $v_{\text{XC}}(\mathbf{r})$ is the corresponding XC potential. This definition also shows that a significant part of $E_{\text{XC}}[\rho(\mathbf{r})]$ is due to correlation effects of the kinetic energy, that is known explicitly only in terms of the reduced 2-particle density matrix [20].

Since up to the exactifying term $E_{\text{XC}}[\rho(\mathbf{r})]$ Eq. (18a) is identical to the HE, it is not surprising that the corresponding Euler-Lagrangian equation

$$\left(-\frac{1}{2}\nabla^2 + v_s^{\text{KS}}(\mathbf{r})\right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (19)$$

also results in a similar fictitious single-particle equation. Since $v_s^{\text{KS}}(\mathbf{r}) = v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) + v(\mathbf{r})$ is the effective potential of an artificial system, such that the ground state density and therewith the energy equals those of the true interacting many-body system. This particular system is therefore called KS system, its effective potential KS potential and the resulting set of self-consistent equations are referred to as KS equations:

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) + v(\mathbf{r})\right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (20a)$$

$$\sum_{i=1}^{N_{occ}} f_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}) = \rho(\mathbf{r}) \quad (20b)$$

$$\frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = v_{\text{XC}}(\mathbf{r}) \quad (20c)$$

At self-consistency it is possible to express $E_0^{\text{KS}}[\rho(\mathbf{r})]$ in terms of the single-particle KS eigenvalues ε_i . Due to the fact that they are not the eigenvalues of the interacting many-body system, but of fictitious non-interacting KS system, $E_0^{\text{KS}}[\rho(\mathbf{r})]$ is merely the sum of ε_i , but

$$E_0^{\text{KS}}[\rho(\mathbf{r})] = \sum_i^{N_{occ}} f_i \varepsilon_i - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} v_{\text{XC}}(\mathbf{r})\rho(\mathbf{r}) + E_{\text{XC}}[\rho(\mathbf{r})]. \quad (21)$$

That is to say that in order to make genuine calculations the KS scheme systematically maps the full interacting many-body problem, with \hat{U} , onto an equivalent fictitious single-body problem, with an effective potential operator $\hat{V}_{\text{KS}} = \hat{U}_s + \hat{V}_H + \hat{V}_{\text{XC}}$, but without \hat{U} [15]:

$$\begin{array}{ccc} \text{TF} & \xrightarrow{E_{\text{XC}}[\rho(\mathbf{r})]} & \text{HK} \\ T_s[\{\psi_i[\rho(\mathbf{r})]\}] \downarrow & & \downarrow T_s[\{\psi_i[\rho(\mathbf{r})]\}] \\ \text{HE} & \xrightarrow{E_{\text{XC}}[\rho(\mathbf{r})]} & \text{KS} \end{array}$$

The Exchange and Correlation Functional

In the previous subsection DFT has been outlined as an exact theory, presuming that the exact XC functional is known. Unfortunately, except for the uniform electron gas [21], this is not the case and one has to resort to more or less accurate approximations. For the sake of brevity, only the main physical principles, as well as the most notable exact properties, rather than the various rungs of "Jacob's ladder to heaven" [22] will be discussed here.

On this account the following break-up is particularly convenient:

$$\begin{aligned} E_{\text{XC}}[\rho(\mathbf{r})] &= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho_{\text{XC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= E_{\text{X}}[\rho(\mathbf{r})] + E_{\text{C}}[\rho(\mathbf{r})], \end{aligned} \quad (22)$$

where $E_{\text{X}}[\rho(\mathbf{r})]$ is the exchange energy due to Pauli repulsion, $E_{\text{C}}[\rho(\mathbf{r})]$ the electron correlation energy and $\rho_{\text{XC}}(\mathbf{r}, \mathbf{r}') = \rho_{\text{X}}(\mathbf{r}, \mathbf{r}') + \rho_{\text{C}}(\mathbf{r}, \mathbf{r}')$ the XC hole. The former is therefore the energy lowering due to the antisymmetry requirement on the wavefunction of a fermionic system and can be exactly calculated in terms of an explicit orbital, or implicit density functional

$$\begin{aligned} E_{\text{X}}[\rho(\mathbf{r})] &= -\frac{1}{2} \sum_{i,j} \int d\mathbf{r} \int d\mathbf{r}' \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r})\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= E_{\text{X}}[\{\psi_i[\rho(\mathbf{r})]\}]. \end{aligned} \quad (23)$$

Eq. (23) is the so called Hartree-Fock exchange energy, but with KS orbitals. However, the nonlocal form of the exact exchange energy comes at a considerable computational burden to solve four-center integrals, which is about two order of magnitude more expensive than is the case for local or semi-local approximations to the exact XC functional. The correlation energy accounts for the additional energy lowering, since electrons with opposite spins also avoid each other. However, contrary to the exchange part, no exact expression for $E_{\text{C}}[\rho(\mathbf{r})]$ is known, neither in terms of orbitals nor densities.

Obviously, DFT would be of little use if one had to know $E_{\text{XC}}[\rho(\mathbf{r})]$ exactly, but luckily it is usually energetically substantially smaller than each the remaining terms, which are known. One can thus hope that reasonable simple approximations to $E_{\text{XC}}[\rho(\mathbf{r})]$, will still allows for qualitatively correct estimates of $E_0[\rho(\mathbf{r})]$, without relying on additional adjustable parameters.

The following properties of the exact XC functional are well established and serves as valuable guides in the construction of approximations to $E_{\text{XC}}[\rho(\mathbf{r})]$. In particular the exact exchange hole $\rho_{\text{X}}(\mathbf{r}, \mathbf{r}')$ obeys the sum rule $\int d\mathbf{r}' \rho_{\text{X}}(\mathbf{r}, \mathbf{r}') = -1$, and since the correlation hole integrates to zero furthermore $\int d\mathbf{r}' \rho_{\text{XC}}(\mathbf{r}, \mathbf{r}') = 0$ is valid.

Another important property of the exact XC functional is that in the one-electron limit the following conditions hold:

$$E_{\text{C}}[\rho^{(1)}(\mathbf{r})] = 0 \quad (24a)$$

$$E_{\text{X}}[\rho^{(1)}(\mathbf{r})] = -E_{\text{H}}[\rho^{(1)}(\mathbf{r})], \quad (24b)$$

where $\rho^{(1)}$ is a one-electron density. These conditions, which are satisfied within the Hartree-Fock approximation, but not by standard local or semilocal XC functionals, ensure that there is no artificial self-interaction of an electron with itself.

The Lieb-Oxford bound [23]

$$E_{\text{X}}[\rho(\mathbf{r})] \geq E_{\text{XC}}[\rho(\mathbf{r})] \geq -1.68 \int d\mathbf{r} \rho(\mathbf{r})^{4/3}, \quad (25)$$

represents a lower bound on the XC energy and is typically fulfilled by the most common XC functionals.

One, if not the most, intriguing property of the exact XC functional, is the derivative discontinuity of the XC functional with respect to the particle number [24–26]

$$\begin{aligned} \Delta_{\text{XC}} &= \left. \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right|_{N_e+\delta} - \left. \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right|_{N_e-\delta} \\ &= v_{\text{XC}}^+(\mathbf{r}) - v_{\text{XC}}^-(\mathbf{r}), \end{aligned} \quad (26)$$

where δ is an infinitesimal shift of N_e , while Δ_{XC} is a system-dependent shift of $v_{\text{XC}}(\mathbf{r})$, which is independent on \mathbf{r} . The noninteracting, single-particle kinetic energy functional obeys a similar discontinuity given by

$$\begin{aligned} \Delta_{\text{KS}} &= \left. \frac{\delta T_s[\{\psi_i[\rho(\mathbf{r})]\}]}{\delta \rho(\mathbf{r})} \right|_{N_e+\delta} - \left. \frac{\delta T_s[\{\psi_i[\rho(\mathbf{r})]\}]}{\delta \rho(\mathbf{r})} \right|_{N_e-\delta} \\ &= \varepsilon_{N+1}(\mathbf{r}) - \varepsilon_N(\mathbf{r}), \end{aligned} \quad (27)$$

where ε_{N+1} and ε_N are again the KS single-particle energies of the lowest unoccupied and highest occupied eigenstate. In the quantum chemistry community

they are denoted as lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), respectively. Therefore, Eq. (27) is nothing but the KS single-particle gap Δ_{KS} , or HOMO-LUMO gap, whereas Eq. (26) is a truly many-body effect. Therefore, the true fundamental gap $\Delta = E(N+1) - 2E(N) + E(N-1)$ is the derivative discontinuity of the exact total energy functional for the ground state [20, 24–26]

$$\begin{aligned}\Delta &= \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \Big|_{N_e+\delta} - \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \Big|_{N_e-\delta} \\ &= \Delta_{\text{KS}} + \Delta_{\text{XC}}.\end{aligned}\quad (28)$$

Since all other terms in $E[\rho(\mathbf{r})]$ are smooth functionals of $\rho(\mathbf{r})$, their derivatives are continuous, so that Δ is only the sum of Eqs. (26) and (27). However, in particular the derivative discontinuity of the XC functional has till now resisted all attempts of describing it within local or semilocal approximations. In fact, standard XC functionals predict $\Delta_{\text{XC}} = 0$, which causes that the fundamental gap is typically underestimated.

AB-INITIO MOLECULAR DYNAMICS

In the following let us assume that the potential energy function is calculated on-the-fly using DFT, so that $\Phi(\mathbf{R}_I) = E[\{\psi_i\}; \mathbf{R}_I] = E^{\text{KS}}[\{\psi_i[\rho(\mathbf{r})]\}] + E_{\text{II}}(\mathbf{R}_I)$. In any case, AIMD [5, 27–31] comes in two fundamental flavors, which are outlined in this section.

Born-Oppenheimer Molecular Dynamics

In Born-Oppenheimer MD (BOMD) the potential energy $E[\{\psi_i\}; \mathbf{R}_I]$ is minimized at every MD step with respect to $\{\psi_i(\mathbf{r})\}$ under the holonomic orthonormality constraint $\langle \psi_i(\mathbf{r}) | \psi_j(\mathbf{r}) \rangle = \delta_{ij}$. This leads to the following Lagrangian

$$\begin{aligned}\mathcal{L}_{\text{BO}}(\{\psi_i\}; \mathbf{R}_I, \dot{\mathbf{R}}_I) &= \frac{1}{2} \sum_{I=1}^N M_I \dot{\mathbf{R}}_I^2 - \min_{\{\psi_i\}} E[\{\psi_i\}; \mathbf{R}_I] \\ &\quad + \sum_{i,j} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}),\end{aligned}\quad (29)$$

where Λ is a Hermitian Lagrangian multiplier matrix. By solving the according Euler-Lagrangian equations

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad (30a)$$

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \langle \psi_i |} = \frac{\partial \mathcal{L}}{\partial \langle \psi_i |} \quad (30b)$$

one obtains the associated equations of motion (EOM)

$$\begin{aligned}M_I \ddot{\mathbf{R}}_I &= -\nabla_{\mathbf{R}_I} \left[\min_{\{\psi_i\}} E[\{\psi_i\}; \mathbf{R}_I] \Big|_{\{\langle \psi_i | \psi_j \rangle = \delta_{ij}\}} \right] \\ &= -\frac{\partial E}{\partial \mathbf{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i | \psi_j \rangle \\ &\quad - 2 \sum_i \frac{\partial \langle \psi_i |}{\partial \mathbf{R}_I} \left[\frac{\delta E}{\delta \langle \psi_i |} - \sum_j \Lambda_{ij} | \psi_j \rangle \right]\end{aligned}\quad (31a)$$

$$\begin{aligned}0 &\lesssim -\frac{\delta E}{\delta \langle \psi_i |} + \sum_j \Lambda_{ij} | \psi_j \rangle \\ &= -\hat{H}_e \langle \psi_i | + \sum_j \Lambda_{ij} | \psi_j \rangle\end{aligned}\quad (31b)$$

The first term on the right-hand side (RHS) of Eq. (31a) is the so called Hellmann-Feynman force. The second term, which is denoted as Pulay [32], or wavefunction force F_{WF} , is a constraint force due to the holonomic orthonormality constraint, and is nonvanishing if and only if the basis functions ϕ_j explicitly depends on \mathbf{R}_I . The final term stems from the fact that, independent of the particular basis set, there is always an implicit dependence on the atomic positions through the expansion coefficient $c_{ij}(\mathbf{r})$ within the common linear combination of atomic orbitals ϕ_j :

$$\psi_i(\mathbf{r}) = \sum_j c_{ij}(\mathbf{r}) \phi_j. \quad (32)$$

The factor 2 stems from the assumption that the KS orbitals are real, an inessential simplification. Nevertheless, the whole term vanishes whenever $\psi_i(\mathbf{r})$ is an eigenfunction of the Hamiltonian within the subspace spanned by the not necessarily complete basis set [33, 34]. Note, that this is a much weaker condition than the original Hellmann-Feynman theorem [35, 36], which we hence haven't availed throughout the derivation, except as an eponym for the first RHS term of Eq. (31a). However, as the KS functional is nonlinear, eigenfunctions of its Hamiltonian \hat{H}_e are only obtained at exact self-consistency, which is why the last term of Eq. (31a) is also referred to as non-self-consistent force F_{NSC} . Unfortunately, in any numerical calculation this can not be assumed, which results in immanent inconsistent forces and to the inequality of Eq. (31b). Neglecting either F_{WF} or F_{NSC} , i.e. applying the Hellmann-Feynman theorem to a non-eigenfunction leads merely to a perturbative estimate of the generalized forces [37]

$$\mathbf{F} = \mathbf{F}_{\text{HF}} + \mathbf{F}_{\text{WF}} + \mathbf{F}_{\text{NSC}}, \quad (33)$$

which, contrary to the energies, depends just linearly on the error in the electronic charge density. As a consequence it is much more exacting to calculate accurate forces than total energies.

However, as a corollary of the BO approximation, the electronic, as well as the ionic subsystems are adiabatically strictly separated from each other, and therefore does not entail any restrictions on the maximum possible integration time step, so that time steps up to the ionic resonance limit are feasible. This actually holds irrespective of the band gap, so as to, at least in principle, even metals can be straightforwardly treated.

Car-Parrinello Molecular Dynamics

In Car-Parrinello MD (CPMD) [27] a coupled electron-dynamics is performed, in which the electronic degrees of freedom are added to the Lagrangian as classical ones:

$$\begin{aligned} \mathcal{L}_{\text{CP}}(\{\psi_i\}; \mathbf{R}_I, \dot{\mathbf{R}}_I) = & \frac{1}{2}\mu \sum_{i=1}^M \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \frac{1}{2} \sum_{I=1}^N M_I \dot{\mathbf{R}}_I^2 \\ & - E[\{\psi_i\}; \mathbf{R}_I] \\ & + \sum_{i,j} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) \end{aligned} \quad (34)$$

Once again, applying the Euler-Lagrangian equations Eq. (30a) and Eq. (30b) entails an EOM, where the electronic degrees of freedom inhere an artificial inertia μ and are propagated within a fictitious Newtonian dynamics, such that the electrons follows the ions adiabatically:

$$\begin{aligned} M_I \ddot{\mathbf{R}}_I = & -\nabla_{\mathbf{R}_I} \left[E[\{\psi_i\}; \mathbf{R}_I] \Big|_{\{\langle \psi_i | \psi_j \rangle = \delta_{ij}\}} \right] \\ = & -\frac{\partial E}{\partial \mathbf{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i | \psi_j \rangle \end{aligned} \quad (35a)$$

$$\begin{aligned} \mu \ddot{\psi}_i(\mathbf{r}, t) = & -\frac{\delta E}{\delta \langle \psi_i |} + \sum_j \Lambda_{ij} |\psi_j\rangle \\ = & -\hat{H}_e \langle \psi_i | + \sum_j \Lambda_{ij} |\psi_j\rangle \end{aligned} \quad (35b)$$

As a consequence of the BO approximation, the high-frequency oscillations of Eq. (35b) vanishes on ionic time scales, so that $\ddot{\psi}_i \simeq 0$. Hence, similar to Ehrenfest dynamics [38], the total derivative of the instantaneous, rather than the fully minimized, expectation value $\langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle$ of the Hamiltonian yields the forces that are consistent with the corresponding energies. This means, that owing to the absence of necessity to fully minimize the energy functional, but rather to simply evaluate it at the instantaneous time step, F_{NSC} is identical zero by its

very definition. Given a sufficiently small fictitious mass, the constant of motion is strictly conserved and errors in the forces are negligible, in particular if the ionic masses are renormalized by a constant mass tensor [39–41]. In this respect CPMD combines most of the vantages of BO and Ehrenfest MD in the sense that the KS functional are only evaluated. There is no need to repeatedly solving it either by diagonalization or, equivalently, iterative minimization. However, due to the finite accuracy of any integrator, the holonomic orthonormality constraint of the orbitals have to be explicitly enforced.

In order to ensure an adiabatic energy-scale separation of the nuclear and the electronic degrees of freedom and to prevent energy transfer between them, the ionic phonon frequency ω_I has to be much smaller than the electronic analog ω_e . As had been suggested in an eminent phenomenological study of Pastore and Buda [42]

$$\omega_e \propto \sqrt{\frac{\Delta E_{\text{gap}}}{\mu}}. \quad (36)$$

As a consequence the maximum integration time step Δt_{max} depends on the inertia like $\sqrt{\mu}$. The same also holds for the deviation from the BO surface [43]

$$|\psi_\mu(\mathbf{r}, t) - \psi_0(\mathbf{r}, t)| \leq C\sqrt{\mu}. \quad (37)$$

Therefore the fictitious mass, although physically completely meaningless, acts as a continuous slider which allows to adjust any desired degree of accuracy, in terms of deviation from the BO surface, reciprocal to the computational efficiency in a well controlled manner.

But if a metallic system is treated, due to the fact that CP states are strictly not KS eigenstates, Eq. (36) is identical zero and either a thermostat for the electronic degrees of freedom [39, 44, 45] to counterbalance the exchange of energy, or an extended functional with fractional occupation numbers [46–49] is necessary.

In the end drawing a proper conclusion, if either BOMD or CPMD is to favour, turns out to be very subtle [50] and depends largely on the definition of accuracy and on the particular application.

AN EFFICIENT AND ACCURATE CAR-PARRINELLO-LIKE APPROACH TO BORN-OPPENHEIMER MD

Even though DFT-based AIMD has been very successful in describing a large variety of physical phenomena, its computational cost has limited the attainable length and time scales in spite of substantial progress. For a while it was believed that linear scaling methods [51–53] could have offered a solution. Unfortunately, the crossover point at which linear scaling methods become

advantageous has remained fairly large, especially if high accuracy is needed [54, 55]. Therefore, it would be very desirable to accelerate ab-initio simulations with up to thousands of atoms, such that simulations as long as a few nanoseconds can be routinely performed, thus making completely new phenomena accessible to AIMD simulations. BOMD, in which the DFT functional is fully minimized at each MD time step, does not seem to offer much room for further improvement. For this reason recently another direction has been followed to improve the efficiency at current system sizes. In the spirit of CPMD [27], some form of dynamics for the electronic degrees of freedom is implemented, which automatically keeps the system close to the instantaneous BO surface, but at variance to the original proposal in a localized orbital representation [56–59]. The acceleration stems on the one hand from this more compact description of the electronic wavefunctions, but is mainly due to the ability to reduce or even fully bypass the aforementioned SCF cycle. Nevertheless, just like in CPMD, these methods suffer from rather short integration time steps. However, rather recently a novel Car-Parrinello-like approach to BOMD has been proposed, which overcomes this limitation and combines the accuracy and long time steps of BOMD with the efficiency of CPMD [60].

From now on the general case will be considered, where the DFT KS orbitals are expanded in a non-orthogonal basis set. Let M be the dimension of the Hilbert space, i.e. the number of basis functions, and \mathbf{S} the $M \times M$ overlap matrix. As usual the expansion coefficients of the N lowest occupied orbitals are arranged in a rectangular $M \times N$ matrix \mathbf{C} . The density matrix can then be written as $\mathbf{P} = \mathbf{C}\mathbf{C}^T$ and must obey the idempotency condition $\mathbf{P} = \mathbf{P}\mathbf{P}$ that is due to the fermionic nature of electrons, which compels the wavefunction to be antisymmetric in order to meet the Pauli exclusion principle. The potential energy surface on which the ions move is defined by the minimum of an appropriately chosen energy functional $E_{\text{DFT}}[\mathbf{C}, \mathbf{R}_I]$, which is expressed as a functional of \mathbf{C} and a function of the ionic coordinates \mathbf{R}_I . In this notation the BO EOM reads as follows:

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \min_{\mathbf{C}} E_{\text{DFT}}[\mathbf{C}, \mathbf{R}_I], \quad (38)$$

where the search for the minimum is restricted to the \mathbf{C} 's that satisfy the orthonormality condition $\mathbf{C}^T \mathbf{S} \mathbf{C} = \mathbf{I}$, which is equivalent to imposing the idempotency condition on \mathbf{P} . As before, the forces of Eq. (38) can be divided into three contributions, (i) the Hellmann-Feynman forces [35, 36], (ii) the Pulay forces [32], which are present whenever the basis set depends on the ionic positions, and (iii) a residual term [37], which is non-zero except when full self-consistency is reached. The last term leads inevitable to a poor energy conservation in BOMD unless a very tight convergence criterion is im-

posed. In Car-Parrinello-like approaches this is circumvented by the design of a coupled electron-ion dynamics, which maintains the system very close to the BO surface, but at the cost of small integration time steps.

Density Matrix Propagation

Based on ideas of the original CP approach it is possible to design an improved dynamics for the coupled system of electrons and ions [60]. However, contrary to the original scheme, this novel method is not expressed as an explicit EOM for the \mathbf{C} 's, but rather as an integration scheme for the electronic degrees of freedom. The knowledge of the previous K values of $\mathbf{C}(t_{n-l})$, where $l \in [1, K]$, determines the value of $\mathbf{C}(t_n)$, such that at any instant of time the \mathbf{C} 's are as close as possible to the instantaneous ground state. As for the short-term integration of the electronic degrees of freedom, accuracy is crucial, a highly accurate and efficient algorithm is required. Therefore, here the always stable predictor-corrector (ASPC) method [61, 62] of Kolafa has been selected. This scheme was originally devised to deal with classical polarization, so that care must be taken that during the evolution the idempotency condition is always satisfied. The modified predictor

$$\begin{aligned} \mathbf{C}^p(t_n) \cong & \sum_{m=1}^K (-1)^{m+1} m \frac{\binom{2K}{K-m}}{\binom{2K-2}{K-1}} \underbrace{\mathbf{C}(t_{n-m}) \mathbf{C}^T(t_{n-m})}_{\mathbf{P}(t_{n-m})} \\ & \times \mathbf{S}(t_{n-m}) \mathbf{C}(t_{n-1}) \end{aligned} \quad (39)$$

uses the extrapolated contra-covariant density matrix $\mathbf{P}\mathbf{S}$ as an approximate projector on to the occupied subspace $\mathbf{C}(t_{n-1})$. In this way, the fact that the physically relevant contra-covariant density matrix $\mathbf{P}\mathbf{S}$ evolves much more smoothly and is therefore substantially easier to predict than \mathbf{C} is ideally utilized. The modified predictor is followed by a corrector step to minimize the error and to further reduce the deviation from the instantaneous ground state. The corrector

$$\begin{aligned} \mathbf{C}(t_n) &= \omega \text{MIN}[\mathbf{C}^p(t_n)] + (1 - \omega) \mathbf{C}^p(t_n), \\ \text{with } \omega &= \frac{K}{2K-1} \end{aligned} \quad (40)$$

consists only of a single preconditioned minimization step $\text{MIN}[\mathbf{C}^p(t_n)]$ of a properly selected minimization procedure. Apparently, the predictor can also be repeatedly applied, in which case the ground state is even more closely approached, but at the cost of additional electronic gradient calculations. However, as will be shown immediately in general this is not necessary. The numerical coefficients of Eq. (39) were selected in order to ensure time-reversibility up to $O(\hbar^{K+2})$, while ω was chosen

to guarantee a stable relaxation towards the minimum. Due to the fact that the energy is invariant under unitary transformations within the subspace of occupied orbitals \mathbf{C} , it must be ensured that this time-dependent gauge transformation is not strongly changed by $\text{MIN}[\mathbf{C}^p(t_n)]$, as in this case continuity between the \mathbf{C} 's may be lost.

Electronic Forces by Orbital Transformations

Moreover, the minimization scheme must be very efficient in bringing the system as close as possible to the instantaneous ground state and at the same time preserves the idempotency condition of the density matrix. For these reasons, the orbital transformation (OT) method of VandeVondele and Hutter [63] has been chosen. Inspired by the form of the exponential transformation [64] an auxiliary variable \mathbf{X} is introduced, to parameterize the occupied orbitals

$$\mathbf{C}(\mathbf{X}) = \mathbf{C}^p(t_n) \cos(\mathbf{U}) + \mathbf{X}\mathbf{U}^{-1} \sin(\mathbf{U}), \quad (41)$$

where $\mathbf{U} = (\mathbf{X}^T \mathbf{S} \mathbf{X})^{1/2}$ and the variable \mathbf{X} has to obey the linear constraint $\mathbf{X}^T \mathbf{S} \mathbf{C}^p(t_n) = 0$. Under this condition $\mathbf{C}(\mathbf{X})$ leads to an idempotent density matrix for any choice of \mathbf{X} , provided that the reference orbitals $\mathbf{C}^p(t_n)$ are orthonormal. Thus, any finite step along the preconditioned gradient direction will exactly fulfill the idempotency constraint by construction. Due to the linear constraint the minimization with respect to \mathbf{X} is performed in an auxiliary tangent space. Since this space is linear, no curved geodesics must be followed, as is the case for variables such as \mathbf{C} that are nonlinearly constrained. In this way, large minimization steps can be taken, especially if a good preconditioner is used [65]. In fact, using an efficient, idempotency conserving direct minimizer such as OT is decisive for the success of this approach. Since the ASPC integrator only approximately preserves the idempotency constraint, it sporadically has to be explicitly enforced, either by a Cholesky decomposition or by single purification iterations [66].

Total Energies and Forces

Having obtained the new wavefunction it is now possible to evaluate the energy and the nuclear forces, which are derived from the following approximate energy functional:

$$E_{\text{PC}}[\rho^p] = \text{Tr}[\mathbf{C}^T H[\rho^p] \mathbf{C}] - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho^p(\mathbf{r})\rho^p(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} V_{\text{XC}}[\rho^p]\rho^p + E_{\text{XC}}[\rho^p] + E_{\text{II}}, \quad (42)$$

where $\rho^p(\mathbf{r})$ is the density associated with $\mathbf{C}^p(t_n)$. $E_{\text{PC}}[\rho]$ can be thought of as an approximation to the Harris-Foulkes functional [67, 68] and maintains the predictor-corrector flavor of this method. The validity of $E_{\text{PC}}[\rho]$ depends only on the efficiency of the minimizer and on the quality of the propagation scheme. The ionic forces are calculated by evaluating the analytic gradient of $E_{\text{PC}}[\rho]$ with respect to the nuclear coordinates. However, as $\Delta\rho = \rho - \rho^p \neq 0$, besides the usual Hellmann-Feynman and Pulay forces an extra term appears:

$$- \int d\mathbf{r} \left\{ \left[\left(\frac{\partial V_{\text{XC}}[\rho^p]}{\partial \rho^p} \right) \Delta\rho + V_{\text{H}}[\Delta\rho] \right] (\nabla_I \rho^p) \right\}, \quad (43)$$

where ρ is the corrected density evaluated using $\mathbf{C}(t_n)$ and ρ^p is the predicted density calculated from $\mathbf{C}^p(t_n)$. Using variational density functional perturbation theory [69, 70], Eq. (43) can be efficiently computed very similar to employing the coupled-perturbed KS scheme. However, due to the fact that usually only a single preconditioned minimization step is performed, $\mathbf{C}(t_n)$ is just an approximate eigenfunction of $H[\rho^p]$ within the subspace spanned by the finite basis set used. This leads to an insignificant error in the forces, provided that $\mathbf{C}(t_n)$ is very close to the ground state.

Modified Langevin Equation

The ability of this dynamics to maintain the system on the BO surface may vary considerably. It is essentially ideal in systems like water, but potentially somewhat less perfect in liquid Si at high temperature, where swift bonding and rebonding processes take continuously place. However, in all cases the dynamics is dissipative, most likely because the employed propagation scheme is not symplectic. Nevertheless, it is possible to rigorously remedy this downward drift if we assume that the forces arising from our dynamics \mathbf{F}_{PC} can be modeled as $\mathbf{F}_{\text{PC}} = \mathbf{F}_{\text{BO}} - \gamma_D \dot{\mathbf{R}}_I$, which, as we shall see immediately, is an excellent assumption. The value of the intrinsic friction coefficient γ_D does not need to be known but it can be bootstrapped by taking a cue from the work of Krajewski and Parrinello [71]. The canonical distribution is sampled by using the following Langevin-type equation

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_{\text{PC}} - \gamma_L \dot{\mathbf{R}}_I + \boldsymbol{\Xi}_I, \quad (44)$$

where M_I is the ionic mass, γ_L is a Langevin friction coefficient and $\boldsymbol{\Xi}_I = \boldsymbol{\Xi}_I^D + \boldsymbol{\Xi}_I^L$ an additive white noise. Using the above assumption Eq. (44) is identically to:

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_{\text{BO}} - (\gamma_D + \gamma_L) \dot{\mathbf{R}}_I + \boldsymbol{\Xi}_I \quad (45)$$

In order to guarantee an accurate sampling of the Boltzmann distribution, the noise has to obey the fluctuation dissipation theorem:

$$\langle \Xi_I(0) \Xi_I(t) \rangle = 6 (\gamma_D + \gamma_L) M_I k_B T \delta(t) \quad (46)$$

The choice of γ_L is arbitrary, while the unknown γ_D has to be determined by requiring that the aggregate noise term generate the correct average temperature, i.e. fulfills the equipartition theorem $\langle \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \rangle = \frac{3}{2} k_B T$. As we see in a moment, this leads to correct a sampling of the Boltzmann distribution. In addition, since the initial dynamics is quite accurate, γ_D is rather small and even dynamical properties can be very well reproduced.

Illustrative Examples: Liquid Silicon, Silica and Water

For the purpose of demonstrating this new approach, it has been implemented in the mixed Gaussian Plane Wave (GPW) [72] code QUICKSTEP [73, 74], which is part of the publicly available suite of programs CP2K [75]. In order to illustrate that this method works well irrespective of band-gap, system size and type, calculations on metallic liquid silicon and liquid silica are presented. Both systems are known to be very difficult, and are examples of liquid metals (Si) as well as of complex, highly polarizable, ionic liquids (SiO_2). Furthermore, the simulations have been performed at 3000 K and 3500 K respectively, which leads to rapidly varying density matrix elements, thus making the propagation of the electronic degrees of freedom particularly challenging. Hence, the selected test cases can be considered as worst-case scenarios for any method.

All simulations have been performed at their experimental liquid densities using double-zeta valence polarization (DZVP) basis sets, adequate density cut-offs, Goedecker-Teter-Hutter pseudopotentials [76–78] and the local-density approximation to the exact exchange and correlation functional. For simplicity the Brillouin zone is sampled at the Γ -point only, while Eq. (45) is integrated using the algorithm of Ricci and Ciccotti [79], with a time step of $h = 1.0$ fs. The friction coefficient γ_L was set equal to zero, while the values for γ_D turned out to be in the range of 10^{-4} fs^{-1} . The new \mathbf{C} 's are predicted using $K = 4$ in Eq. (39), which ensures time-reversibility up to $O(h^6)$.

First, the accuracy in terms of the energetical deviation from the BO surface is considered. As can be seen in FIG. 1 the energies are an upper bound to the ground state and are displaced by a very small and approximately constant amount. It is also shown that, as already mentioned, the deviation from the BO surface can be even further reduced by increasing the number of corrector steps. In fact, it is actually possible to control the

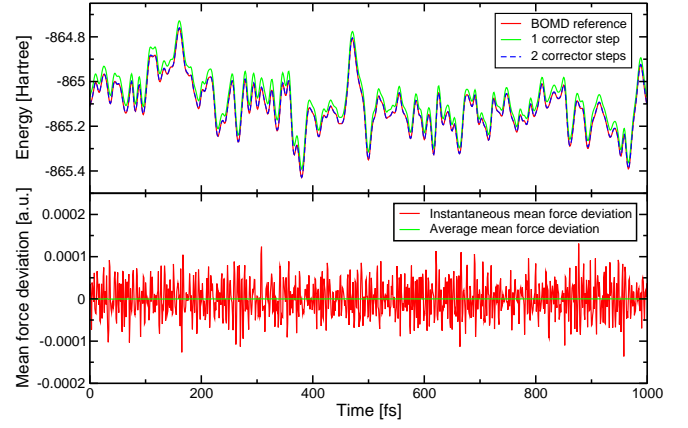


FIG. 1. Deviations from the BO surface of liquid SiO_2 with respect to total energies (upper panel) and mean force deviations (lower panel). The deviation in the energies corresponds to a constant shift of 4.16×10^{-4} Hartree per atom for one corrector step and 3.5×10^{-5} Hartree per atom for two corrector steps. The average mean force deviation is unbiased.

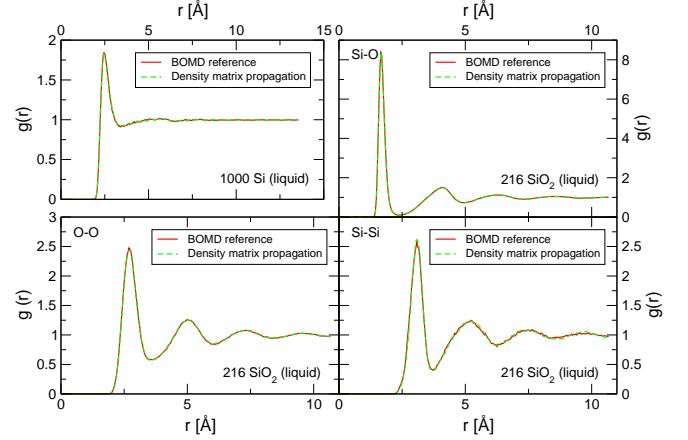


FIG. 2. Partial pair-correlation functions $g(r)$ of liquid Si (upper left panel) and liquid SiO_2 at 3000 K and 3500 K respectively, using a DZVP Gaussian basis set.

deviation from the BO surface by varying the number of corrector steps in order to achieve a preassigned accuracy level. However, in the following only simulations based on a single corrector step will be reported.

Nevertheless, let us now turn to more realistic problems such as those shown in FIG. 2. Although these simulations have been performed with only a single corrector step, they are still amazingly close to the BOMD reference results. It should be emphasized that even in liquid Si, which is metallic and poses problems when using an ordinary CP scheme, a single corrector step is sufficient. This establishes the efficiency of this method, since only a single preconditioned gradient calculation with no additional minimization step has to be performed. The possible acceleration, in comparison with regular BOMD calculations, depends crucially on the system studied. In

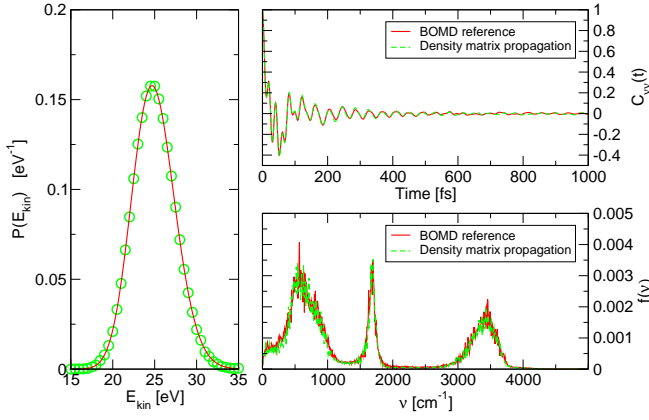


FIG. 3. The kinetic energy distribution calculated from a 1 ns trajectory with a time step of 3.25 fs of metallic liquid Si_{64} using a DZVP Gaussian basis set and a density cutoff of 100 Ry (left panel). Velocity autocorrelation function (upper right) and its Fourier transform (lower right) of 32 Water at 325 K using a TZV2P Gaussian basis set, a density cutoff of 280 Ry and the BLYP exchange-correlation functional. The Langevin friction coefficients are $\gamma_L = 0$ and $\gamma_D \sim 10^{-8} \text{ fs}^{-1}$.

the undoubtedly difficult cases just presented a speed-up of two orders of magnitude compared to using a pure extrapolation scheme have been observed. For simpler problems still an increase in efficiency of at least one order of magnitude can be expected.

In FIG. 3 displays results, which prove that also dynamical properties can be evaluated with accuracy. To that extend the velocity autocorrelation function and its Fourier transform at 325 K is presented. The results are in good agreement with accurate reference calculations and are consistent with experiment, as well as ab-initio all-electron calculations [80], showing that in spite of the stochastic nature of Eq. (45) dynamical properties can also be simulated. This implies, that also chemical reactions and even non-equilibrium processes can be treated. In the same picture it is explicitly verified that the previous assumptions are justified, and indeed a canonical sampling is performed, by showing that the kinetic energy distribution is Maxwellian distributed. To this end, a 64 atom liquid Si simulation is carried out for as long as 1 ns, to reduce the noise and to ensure a proper sampling of the relevant kinetic energy distribution tails.

Due to space considerations only a fraction of the systems studied is reported here. Nevertheless, in all cases this method has proven to be accurate and the gain in speed has always been remarkable [81–86]. Structure relaxation via dynamic annealing and geometry optimization have also been successfully performed [87–92]. Contrary to CPMD and related methods integration time steps up to the ionic resonance can be used. Thanks to this development it is now possible to perform AIMD simulations on medium-sized systems up to a few nanoseconds, thus making a new class of problems accessible to

ab-initio simulations.

CONCLUSION

To conclude it should be noted, that with increasing length and time scales CPMD-based approaches are expected to become more advantageous than BOMD, since otherwise meeting the more and more stringent accuracy requirements of longer simulations and larger system sizes would entail an ever tighter wavefunction convergence. The Car-Parrinello-like approach to BOMD [60] just described extends the scope of ab-initio simulations by combining the best of either method and allows for AIMD simulations previously thought not feasible.

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